CEEDO-TR-78-12

② LEVEL Ⅱ

STUDIES ON EVAPORATION OF HYDRAZINE AND PROCEDURES FOR CLEANUP OF SMALL SPILLS

THOMAS B. STAUFFER

ARLAND W. EYL

ENVIRONMENTAL CHEMISTRY DIVISION

ENVIRONICS DIRECTORATE

D D C

R͟E͟C͟E͟I͟V͟E͟D
FEB 15 1979

B

AUGUST 1978
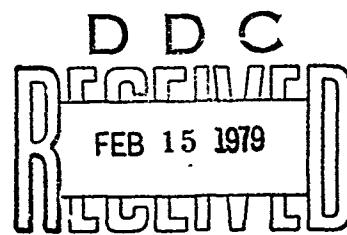
FINAL REPORT FOR PERIOD JUNE 1977 TO JULY 1978

CIVIL AND ENVIRONMENTAL ENGINEERING DEVELOPMENT OFFICE

(AIR FORCE SYSTEMS COMMAND)

TYNDALL AIR FORCE BASE

FLORIDA 32403

79 02 12 040

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CEEDO-TR-78-12	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Studies on Evaporation of Hydrazine and Procedures for Cleanup of Small Spills		5. TYPE OF REPORT & PERIOD COVERED Final Report June 1977 – July 1978 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas B. Stauffer Arland W. Eyl, Jr.		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Det 1 (CEEDO) ADTC Environics Directorate Tyndall AFB FL 32403		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element: 63723F JON: 21037C13
11. CONTROLLING OFFICE NAME AND ADDRESS Det 1 (CEEDO) ADTC/ECC Tyndall AFB FL 32403		12. REPORT DATE August 1978 13. NUMBER OF PAGES 48
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC
RECEIVED
FEB 15 1979
B

18. SUPPLEMENTARY NOTES

Available in DDC.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrazine Fuels	Fuel Spill Cleanup	Environmental Quality
Hydrazine	Missile Fuels	Environics
Monopropellant	H-70 Fuel	Environmental Chemistry
Hydrazine Evaporation	Toxic Materials	F-16 Aircraft

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The evaporation rates of hydrazine (N_2H_4) from pools of the neat fuel and from aqueous solutions were measured under various environmental conditions. Hydrazine continues to evaporate for long periods of time (several days) even from solutions as dilute as 25-percent N_2H_4. Solutions of hydrazine appear to absorb carbon dioxide from the atmosphere. Carbon dioxide gas also suppresses evaporation of hydrazine from concrete surfaces. Procedures are outlined for cleanup and decontamination of small spills of hydrazine in the flightline area. Calcium hypochlorite (HTH), sodium hypochlorite solution (household bleach), and

DD FORM 1473
1 JAN 73

393 750

Cont

hydrogen peroxide with copper catalyst were evaluated for use as possible oxidants to treat dilute hydrazine solutions. Although all three give satisfactory results, either HTH or household bleach is recommended because of availability and ease of use.

PREFACE

This report documents work performed during the period from June 1977 to June 1978 under Program Element 63723F, Project 2103, subtask 7C13. This work was performed by Thomas B. Stauffer and Arland W. Eyl, Jr in response to a request from ASD/YPL for assistance in developing and evaluating procedures for control and cleanup of spills of hydrazine fuel resulting from handling and storage of H-70 fuel (70 percent hydrazine in water) for the F-16 emergency power unit.

This report has been reviewed by the information office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

THOMAS B. STAUFFER
Research Chemist

MICHAEL G. MACNAUGHTON
Maj, USAF, BSC
Chief, Envmtl Sciences Div

PETER A. CROWLEY
Maj, USAF, BSC
Director of Environics

JOSEPH S. PIZZUTO
Colonel, USAF, BSC
Commander

i
(The reverse of this page is blank)

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SECTION I

INTRODUCTION

Hydrazine (N_2H_4) and its salts are used as reducing agents, antioxidants, corrosion inhibitors, oxygen scavengers, agricultural chemical intermediates, and jet and rocket fuels (Reference 1). In solution, it forms a base which is weaker than ammonia. However, more concentrated solutions can be prepared with N_2H_4 than ammonia; therefore, it can be regarded as a caustic solution. In the pure vapor state, hydrazine can autodecompose from catalytic effects or electric spark at such a rapid rate as to cause an explosion (Reference 2).

Hydrazine is a toxic chemical that can be ingested or absorbed through the skin. The National Institute for Occupational Safety and Health (NIOSH) recommends extreme caution in handling hydrazine to reduce the risk of cancer induced by this chemical. NIOSH proposed standards state that work place air concentrations should be controlled so that employees are not exposed to concentrations greater than 0.04 mg/m^3 or 0.03 ppm during any 15-minute sample period (Reference 3).

The Air Force currently uses hydrazine in several rockets and missiles and in the emergency power unit (EPU) of the F-16. Since the F-16 will be used by the North Atlantic Treaty Organization (NATO) countries, the EPU and its associated hydrazine will be distributed worldwide. Servicing of this power unit will require handling hydrazine providing ample opportunity for spills and personnel exposure.

This report furnishes quantitative information on the evaporation of the neat hydrazine fuel and aqueous solutions of the fuel. Volatilization from concrete surfaces was also studied and is reported here. Recommendations for spill cleanup and detoxification are also included.

1

SECTION II

EXPERIMENTAL METHODS

Hydrazine is a colorless, hygroscopic liquid at room temperature.
It has the following physical properties: melting point, $1.53^{\circ}C$;
boiling point, $114.2^{\circ}C$; specific gravity, 1.004; and vapor pressure of
liquid, 14.2 mm Hg at $25^{\circ}C$ (Reference 4). Aqueous solutions of hydrazine
form weak bases and concentrated solutions are quite caustic.

Analytical Techniques

Three different analytical techniques were adapted for use in this
study: (1) Potassium iodate titration was used as a general method for
nonspecific reducing characteristics; (2) reaction with paradimethyl-
aminobenzaldehyde (PDAB) to form a colored azo complex was used for
trace analysis in pure systems; and (3) hydrazine specific analyses wer·
conducted by pyrazole-derivative gas chromatography.

(1) In the potassium iodate (KIO_3) technique (Reference 5) a
0.025M primary standard solution of KIO_3 is prepared. A sample aliquot
is placed in a 125-ml erlenmeyer flask and a mixture of 30-ml of concen-
trated hydrochloric acid (HCl), 20 ml of distilled water, and 5 ml of
chloroform is added. The solution is stoppered with a glass stopper,
shaken and the phases allowed to separate. The titration is continued
in this manner until the wine red organic layer is completely discolored.
The colorless organic layer indicates the end point of the reaction.
The reaction for this titration is shown in Equation (1).

$$IO_3^- + N_2H_4 + 2H^+ + Cl^- \longrightarrow ICl + N_2 + 3H_2O \qquad (1)$$
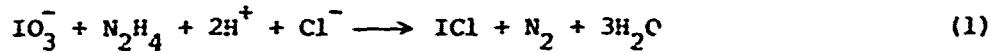
(2) The PDAB technique is based on an observation by Pesez and
Petit (Reference 6) that PDAB and N_2H_4 in a dilute hydrochloric acid
solution turns yellow. Watt and Chrisp (Reference 7) developed a

complete procedure for the analysis of N_2H_4 based on Pesez and Petit's observation. The procedure used in this study was that developed by Watt and Chrisp but further modified in that the 4.0 g of the PDAB is dissolved in 100 ml 2N H_2SO_4. Two milliliters of this solution is added to a 25-ml volumetric, mixed with a sample aliquot, diluted to volume, and the Absorbance measured at 460 nm. PDAB (Fisher Scientific Company) was used directly as received. Absorbances were measured in a 1.0-cm pyrex cell with a Coleman 55 Spectrophotometer. Figure 1 shows a typical calibration curve for the procedure.

(3) The last method of hydrazine analysis is pyrazole-derivative gas chromatography (Reference 8). In this method, hydrazine is reacted with 2,4-pentanedione to form 3,5-dimethylpyrazole as shown in Equation (2).

$$CH_3 - \overset{O}{\underset{||}{C}} - CH_2 - \overset{O}{\underset{||}{C}} - CH_3 + N_2H_4 \longrightarrow CH_3-C \underset{N}{\overset{HC}{\diagdown}} \overset{C-CH_3}{\underset{||}{\underset{N}{\diagup}}} + 2H_2O \qquad (2)$$
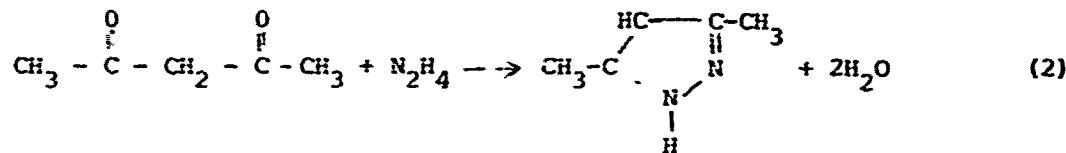
The pH of the sample is adjusted to between 6 and 9 with 1N NaOH or 1N H_2SO_4. The sample is then diluted to 100 ml, 100 μℓ of 2,4-pentanedione are added, and then allowed to react for one hour before chromatography. The samples were then chromatographed on a Tracor Model 222 Gas Chromatograph (GC) equipped with dual flame ionization detectors. Separations were carried out on a 1.83-m by 0.635-cm outside diameter glass U-tube packed with a 30-percent load of a mixture containing 83-percent Apiezon L and 17-percent Amine 220. Nitrogen was the carrier gas with a flow rate of 30-ml per minute. The injector temperature was 225°C, the detector 240°C and the column 160°C isothermal. A sample size of 2.0 μℓ was used for all studies.

Quantitative recovery was checked by preparing standard solutions of hydrazine sulfate and treating with 2,4-pentanedione. These samples were chromatographed, and peak heights were obtained. Standards were also prepared directly from 3,5-dimethylpyrazole, m.p. 107.5-108.5°C,

3
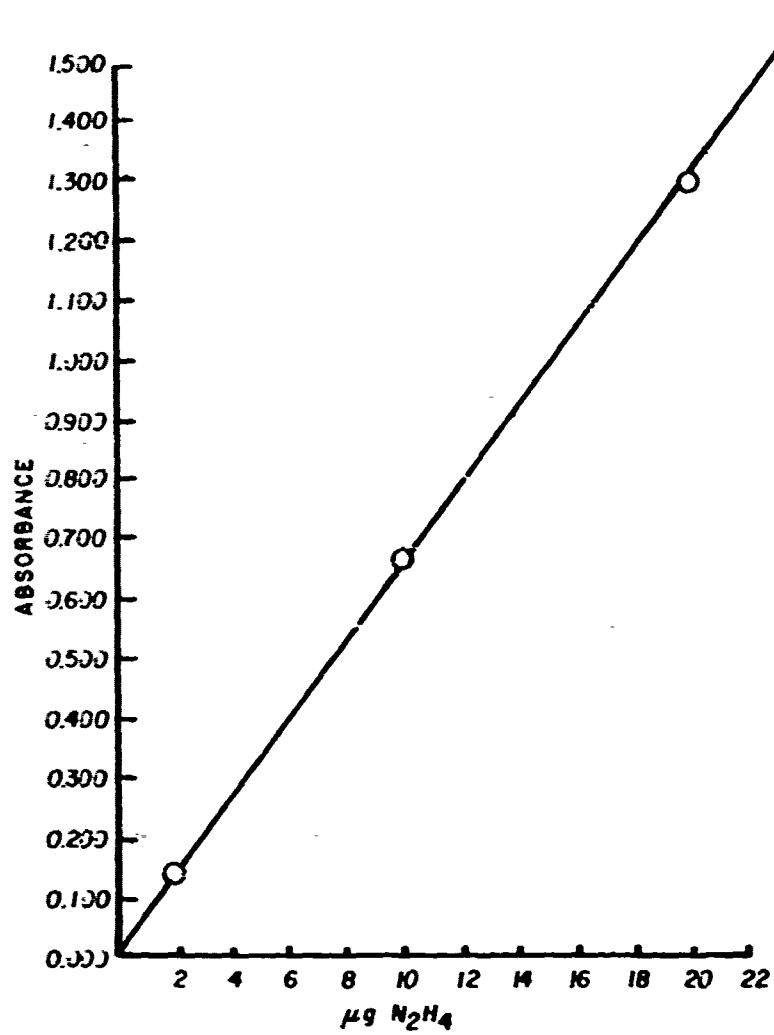
Figure 1. Standard Curve for PDAB Analysis of
Hydrazine

4

and chromatographed to obtain peak heights. Since there was no difference in peak height between similar standards prepared by either method, the derivatization procedure was considered acceptable.

Evaporation Studies

Evaporation studies were conducted on both the neat fuel obtained from Rocky Mountain Arsenal and aqueous solutions ranging from 75 percent (V/V) to 25 percent (V/V) hydrazine. Studies of the neat fuel included work on samples placed outside under prevailing environmental conditions and work on samples under more controlled conditions in the laboratory. Only laboratory studies were conducted on the aqueous solutions.

A known volume of hydrazine was placed in round, 9.0 cm (63.6 cm^2) diameter glass petri dishes and placed outdoors to evaporate. Samples were weighed prior to introduction to the prevailing environmental conditions. At different time intervals the samples were returned to the laboratory, weighed, and the density and N_2H_4 concentration determined.

The laboratory studies duplicated the outdoor studies except the temperature and air velocity were controlled. The temperature was $21\pm1^{\circ}C$ and the air velocity at the evaporating surface was measured with a velometer to be 63.5 cm/sec. The petri dishes were again filled with a known volume of hydrazine or aqueous hydrazine solution and allowed to evaporate. At various time intervals during the evaporation period, the samples were weighed and aliquots removed for analysis.

N_2H_4 volatility from concrete surfaces was studied using the apparatus shown in Figure 2. This apparatus forms an air tight chamber permitting a carrier gas to flow onto the concrete surface and conduct any vapors out. The chamber itself was built by attaching a piece of plexiglass by means of an o-ring and flange to a 15-cm diameter (ID) piece of pyrex pipe. The sample was then placed in this vessel and a

5
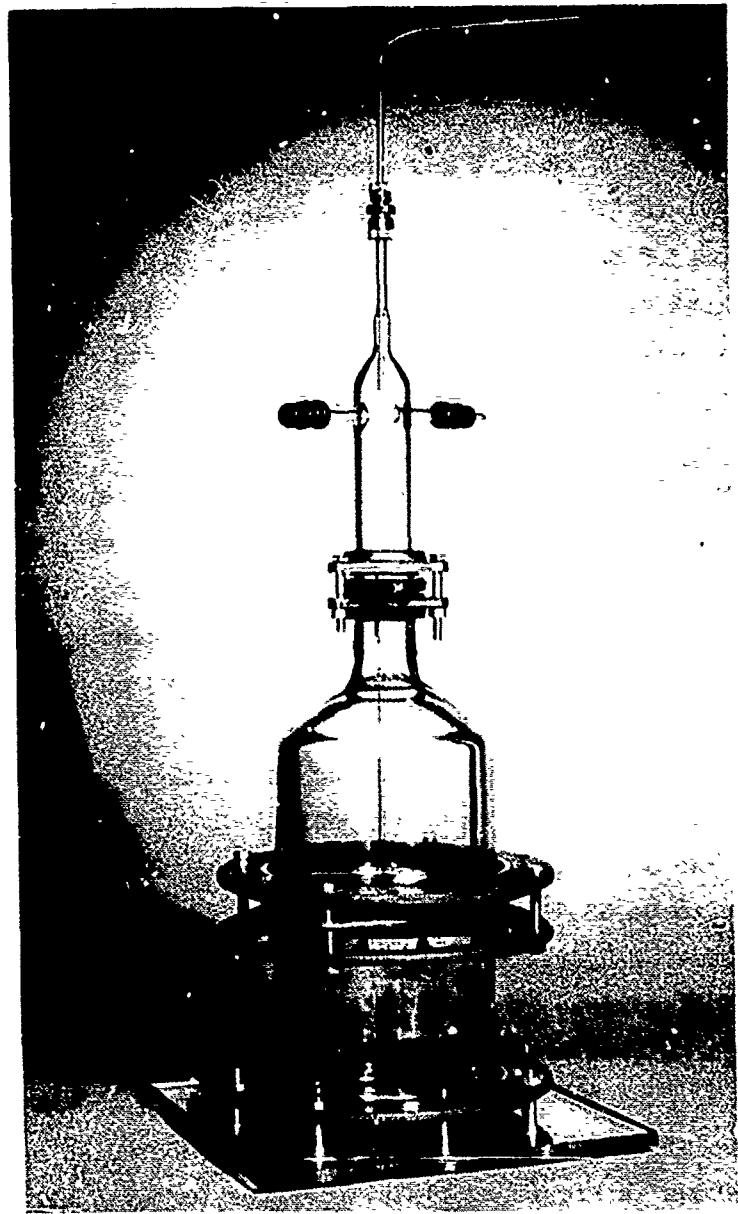
Figure 2. Volatilization Chamber

6

necked-down glass pipe bolted in place over the sample with a flange and teflon seal. The necked-down portion provided two ports for inletting carrier gas and sample gas removal. A glass tube of 4 mm O.D was inserted through the inlet port to approximately 75 mm above the concrete surface and attached to the carrier gas by an ultra-torr fitting. A line was attached between the exit port and a gas wash bottle containing 100 ml of 0.1N H_2SO_4. Evaporated hydrazine was absorbed by the H_2SO_4, and the solution was analyzed for N_2H_4 concentration.

Several comparative studies were performed using the apparatus described in Figure 2. The influence of air, nitrogen gas (N_2G), and carbon dioxide (CO_2) as carrier gases for evaporation was studied. Volatility differences between neat fuel in glass containers and fuel on concrete surfaces were also studied, and the feasibility of using special wipes to clean up small spills on concrete was also evaluated.

A polypropylene felt obtained from GAF Corporation (Cat No 62P019/ 110 sp) and recommended by NASA was tested for use in cleaning up small N_2H_4 spills (less than 2.0 liters). The felt was tested for actual absorption capacity by weighing a known area of felt before and after saturation with N_2H_4. Attempts were also made to wipe up small quantities of hydrazine placed on concrete. These latter experiments were conducted by placing 2.0 ml of 75-percent V/V N_2H_4 solution on a round concrete surface of 81.7 cm^2, and then, after 5 minutes, mopping the surface with a 25.8 cm^2 square of felt. The core surface was then rinsed with one liter of distilled water, and the resulting solution was analyzed for hydrazine concentration. The felt was then placed in distilled water for several minutes, and the N_2H_4 concentration of the resulting solution was determined. A mass balance on these components could be used to determine how much N_2H_4 was left on the concrete surface. After wiping with the felt, the contaminated concrete was placed in the volatilization chamber (Figure 2) and gas was blown over the surface to measure any residual hydrazine which could volatilize.

7

Treatment of Dilute Hydrazine Solutions

Several chemicals were evaluated as potential oxidants for treating dilute waste solutions containing hydrazine. These were 5 percent sodium hypochlorite solution (common household bleach), solid calcium hypochlorite (commercial HTH), and hydrogen peroxide solution (30 percent W/W, Fisher Scientific).

In each test a one-percent hydrazine (V/V) solution was placed in a 500-ml beaker and stirred continuously with a magnetic stirrer. Small aliquots of the oxidizing agent were added to the hydrazine solution. The temperature of the solution was monitored, and samples were withdrawn for hydrazine analysis by the PDAB technique. Enough oxidizing agent was added to provide a 10-percent excess over the hydrazine initially present. Observations were made as to the effectiveness, safety, and convenience of use of the various oxidants.

8

SECTION III

RESULTS

Evaporation Studies

The petri dishes placed outside contained approximately 10 g of N_2H_4. The dishes were placed on a laboratory cart about 1 m above ground level. Figure 3 shows a plot of the mass of N_2H_4 remaining versus time. The data shown were collected on four different days as indicated by the different symbols. The most rapid evaporation rate observed resulted in a loss of 9.4 g N_2H_4 in 180 minutes, whereas the slowest rate showed a loss of 6.1 g in that same time. It became apparent that the liquid remaining after several hours was more viscous than the original hydrazine. Observation of the small volumes remaining after evaporation showed an oily or syrupy consistency.

Two series of tests were conducted outdoors in the shade. In Figure 4 the results of these two runs are plotted showing the mass of N_2H_4 left versus time. In 180 minutes, 4.2 g of hydrazine or 43 percent of the total had evaporated.

Studies conducted inside with controlled temperature and air velocity with neat fuel showed a loss of 7.6 g of hydrazine in the first 180 minutes (Figure 5). The concentration was monitored periodically for another 45 hours, and at the end of this period 8 g of hydrazine remained. In Table 1, evaporation time, average N_2H_4 mass in sample as determined by GC and KIO_3 titrimetry, density, and sample weight for a typical run are given. From Table 1, it can be seen that even though N_2H_4 continued to evaporate over the entire period, the weight and density of the samples increased. The increasing density was attributed to the hydrazine absorbing CO_2 from the atmosphere. To validate this assumption CO_2 was bubbled through a 70 percent (V/V) hydrazine water solution and increase in weight followed. Figure 6 shows a plot of the absorption of CO_2 by the hydrazine solution. When the solution stopped

9
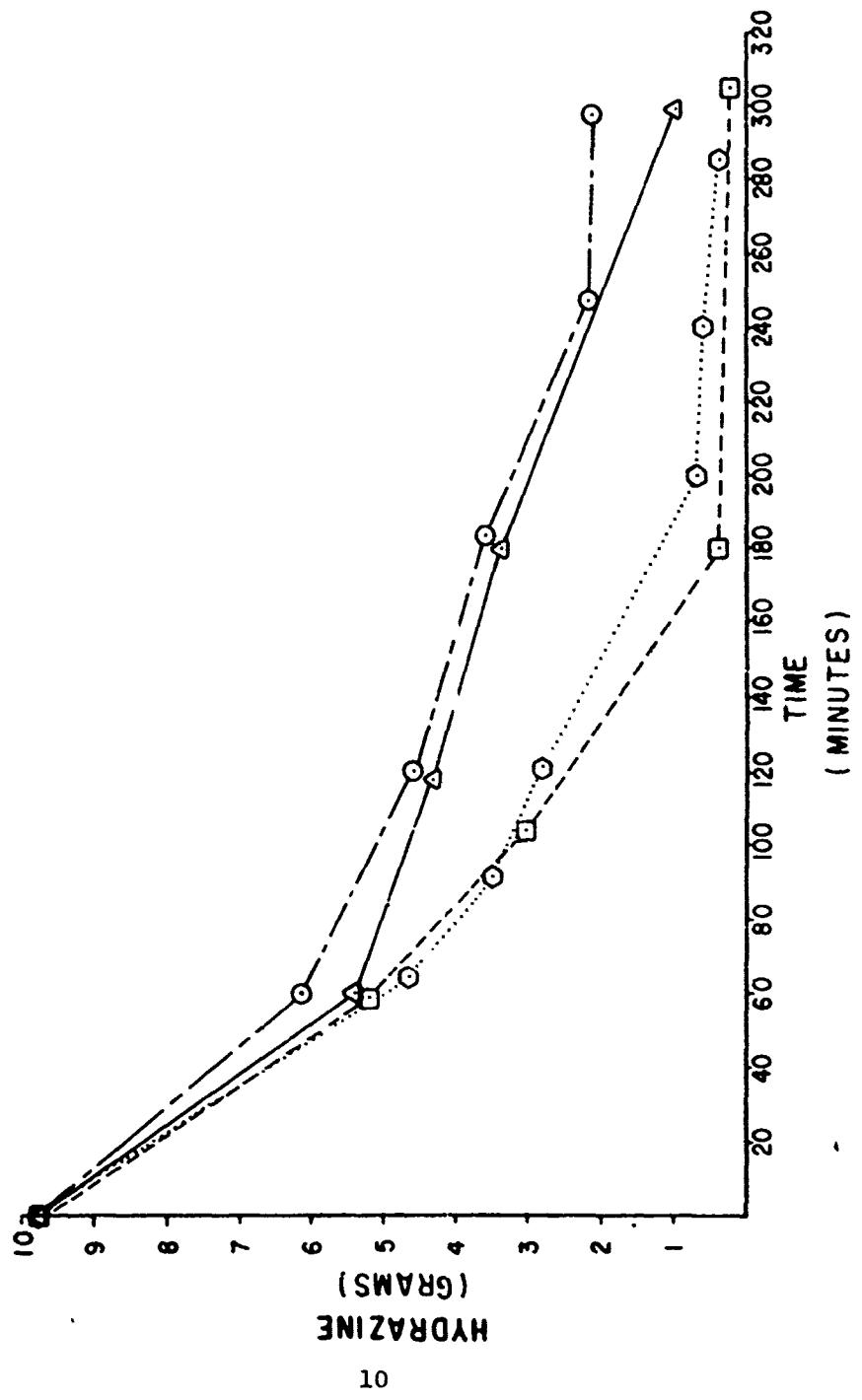
Figure 3. Hydrazine Evaporation Sunshine
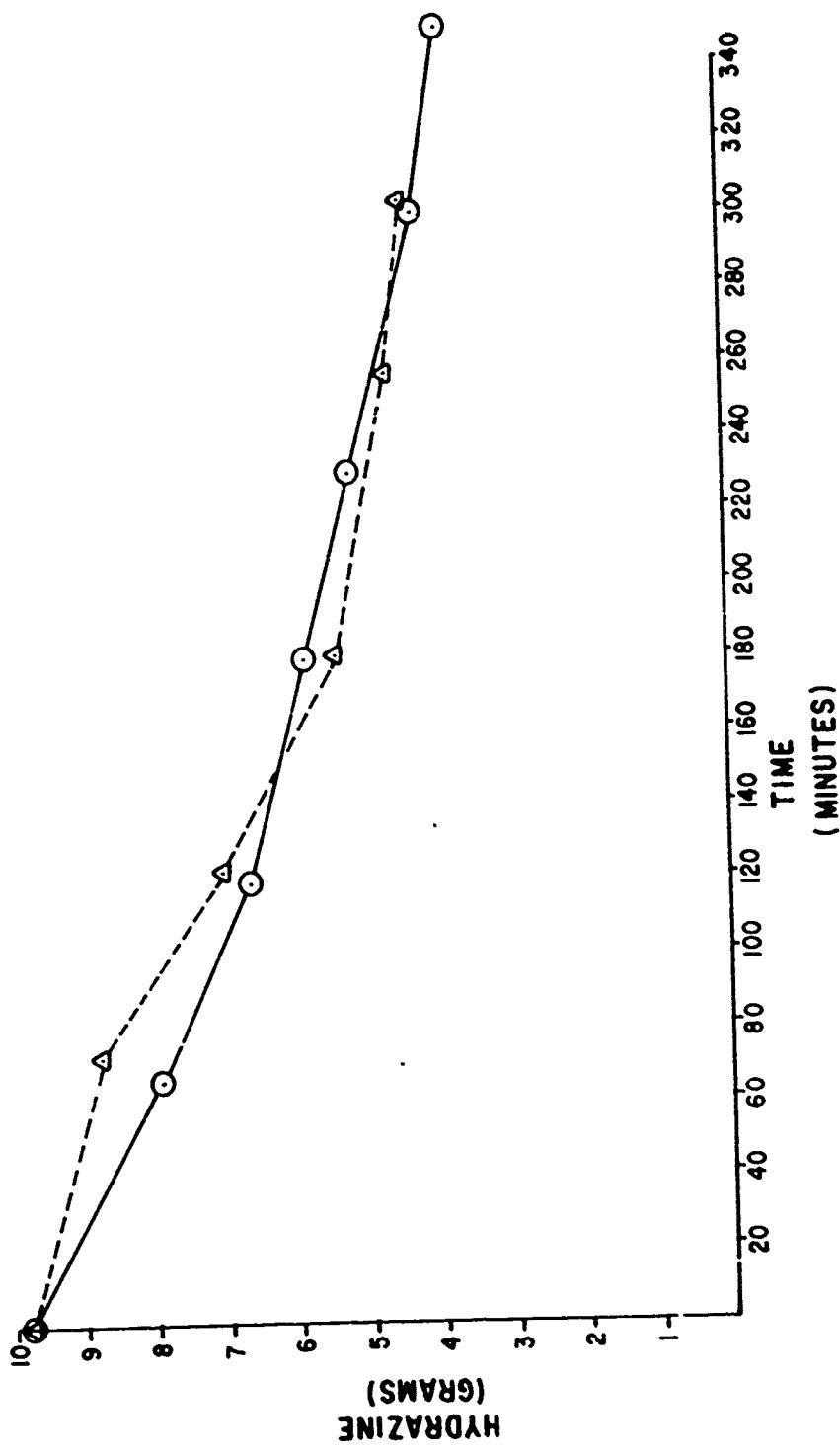
Figure 4. Hydrazine Evaporation Shade

11
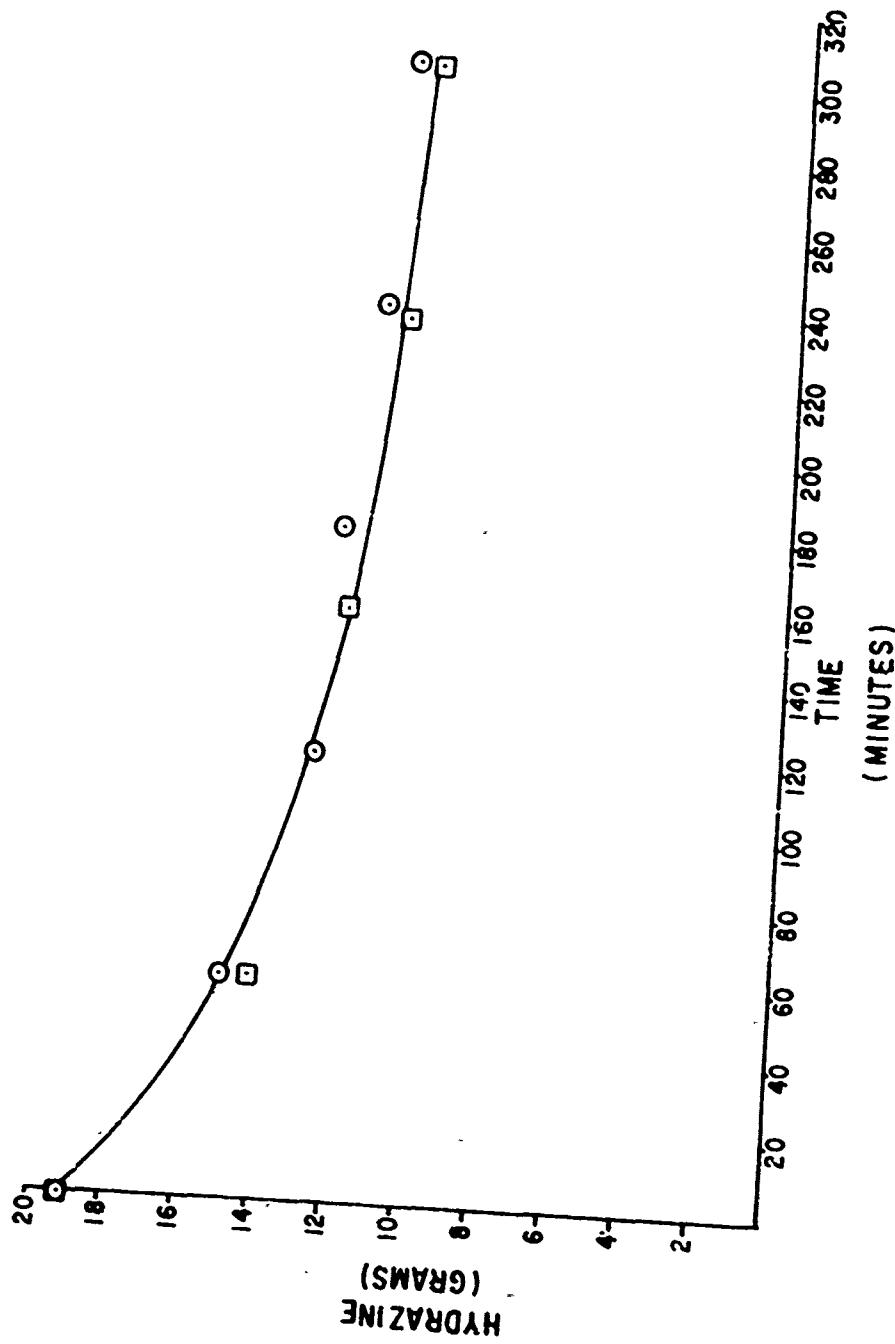
Figure 5. Hydrazine Fuel Evaporation

12
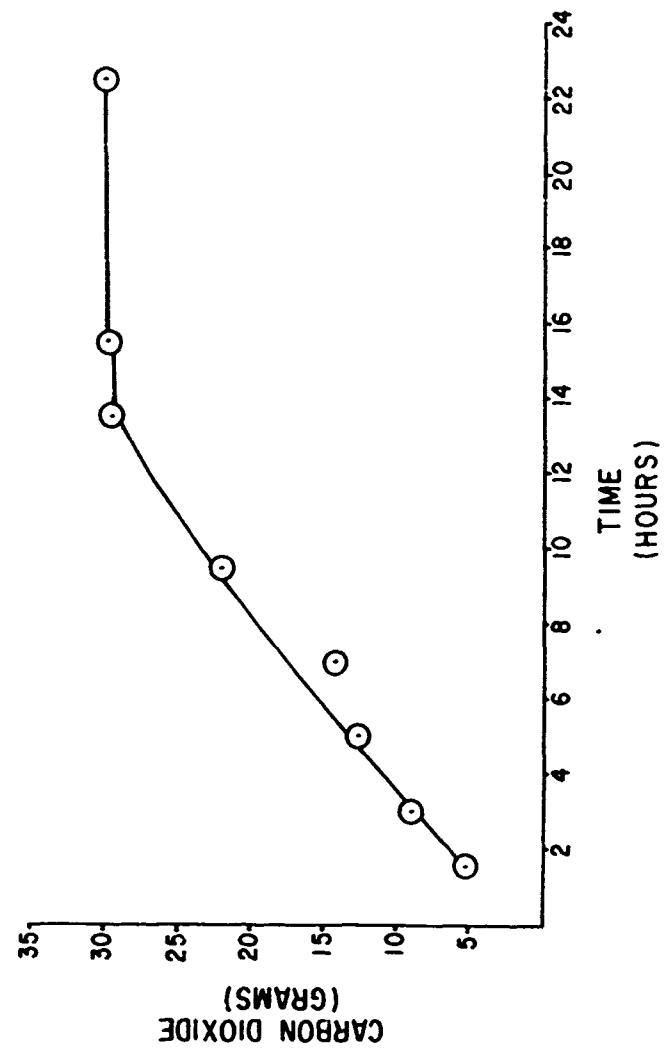
Figure 6. Carbon Dioxide Absorption by 70 Percent (V/V) Solution

13

TABLE 1. EVAPORATION OF NEAT HYDRAZINE FUEL

TIME (min)	N_2H_4 (g)	DENSITY (g/ml)	SAMPLE WEIGHT (g)
0	19.0	1.06	20.16
60	15.0	1.10	19.64
120	12.7	1.09	20.05
180	12.1	1.09	21.03
240	11.2	1.11	22.09
305	10.7	1.09	23.17
360	10.3	1.09	23.88
421	10.2	1.10	24.65
1440	8.9	1.12	32.99
1800	8.7	1.13	33.28
2880	8.1	1.17	33.09

14

gaining weight the experiment was terminated. During the absorption period, 49.96 g of the 70-percent solution absorbed 30.14 g of CO_2 turning to a white semi-solid consistency.

Figure 7 displays the effect of concentration on hydrazine evaporation. The solution concentrations ranged from neat fuel to a 25-percent aqueous solution, as illustrated by the different symbols. It is clear that as the concentration of N_2H_4 in the aqueous solution decreases the evaporation rate is slower. However, it should be noted that the hydrazine continued to evaporate in all cases, and as illustrated in Table 2, even over extended periods of 4 to 5 days, hydrazine continued to volatilize.

Figure 8 represents a long-term study of neat fuel evaporation over a period of nine days. Again there is a rapid initial loss followed by continuous evaporation at a much slower rate. Density increased over the entire run whereas actual sample weight increased for the first day and then slowly decreased for the next 8 days.

Studies using the volatilization chamber (Figure 2) were conducted using air, nitrogen, and carbon dioxide as carrier gas. The mass of hydrazine evaporated from the liquid versus the volume of gas flowing through the chamber are plotted in Figure 9. It is readily apparent that very little of the hydrazine was evaporated by the CO_2. In this study nitrogen volatilized more hydrazine than air.

Evaluation of Felt Wipes

In studies to evaluate the felt material for spill cleanup a 25.3 cm section of material absorbed 7.00 g of the 75 percent V/V aqueous hydrazine solution, giving a capacity of about 0.27 g/cm. Desorbing felt squares deliberately contaminated with 2.0 mls of the 75-percent solution yielded recoveries of 94.5 to 96.5 percent. In the subsequent studies of cleanup, this was considered essentially quantitative recovery,

15
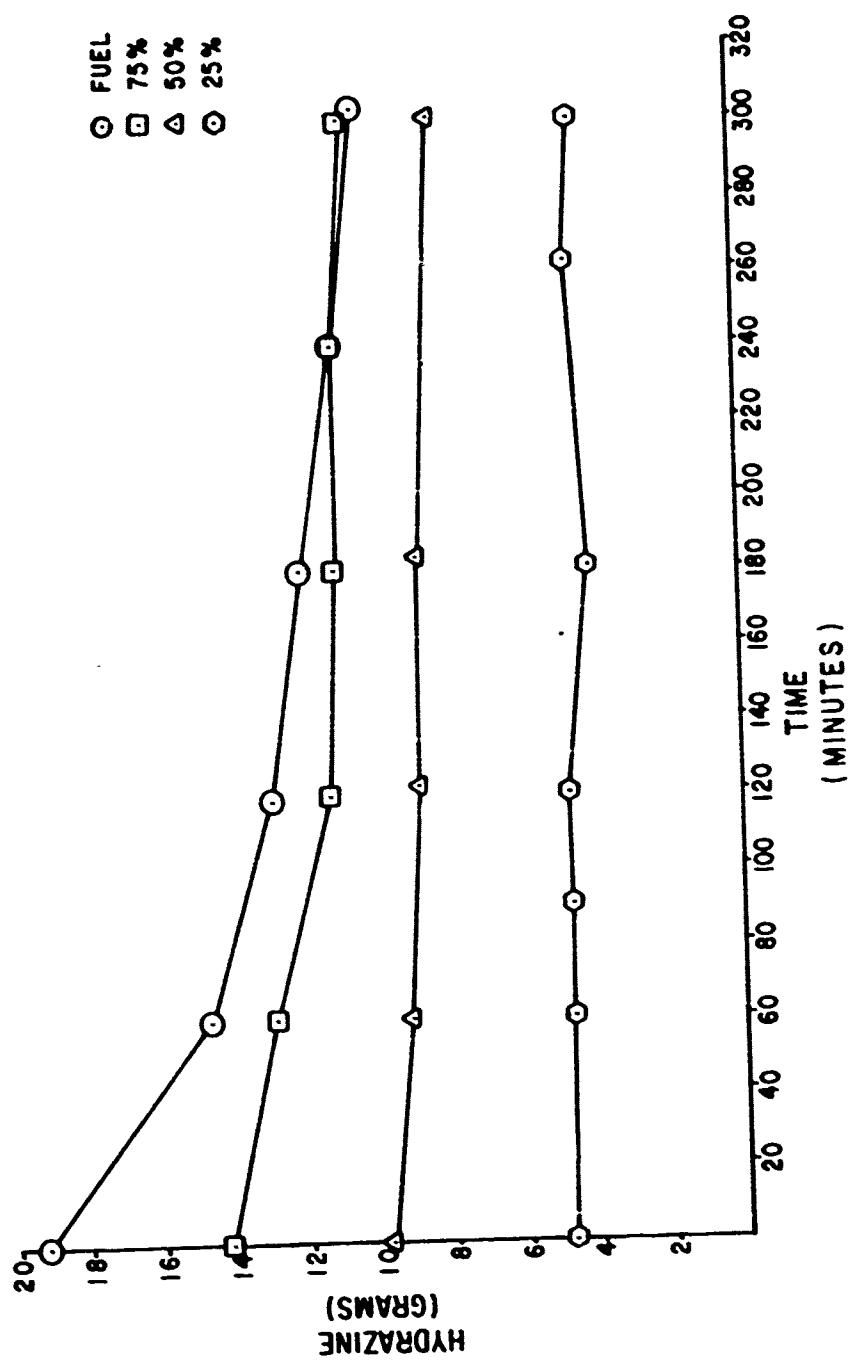
Figure 7. Influence of Concentration on Hydrazine Evaporation

TABLE 2. EVAPORATION OF HYDRAZINE SOLUTIONS

NEAT FUEL

TIME (hr)	N_2H_4 (g)	DENSITY (g/ml)	SAMPLE WEIGHT (g)
0	19.0	1.06	20.16
3	12.1	1.09	21.03
6	10.3	1.09	23.86
24	8.9	1.12	32.99
30	8.7	1.13	33.28
48	8.1	1.17	33.09

75% SOLUTION

TIME (hr)	N_2H_4 (g)	DENSITY (g/ml)	SAMPLE WEIGHT (g)
0	14.4	1.07	19.95
3	11.3	1.08	23.00
6	10.0	1.10	25.18
24	9.0	1.11	31.96
97	8.3	1.19	33.14

50% SOLUTION

TIME (hr)	N_2H_4 (g)	DENSITY (g/ml)	SAMPLE WEIGHT (g)
0	9.4	1.05	19.89
2	8.7	1.06	21.51
6	8.0	1.08	23.46
49	7.9	1.16	24.93
72	7.1	1.18	22.55
170	5.9	1.17	20.14
216	5.4	1.20	16.90

25% SOLUTION

TIME (hr)	N_2H_4 (g)	DENSITY (g/ml)	SAMPLE WEIGHT (g)
0	4.8	1.04	19.82
2	4.8	1.05	19.76
6	4.5	1.06	19.27
24	3.9	1.12	17.07
121	3.9	1.15	12.00
168	2.0	1.17	9.07
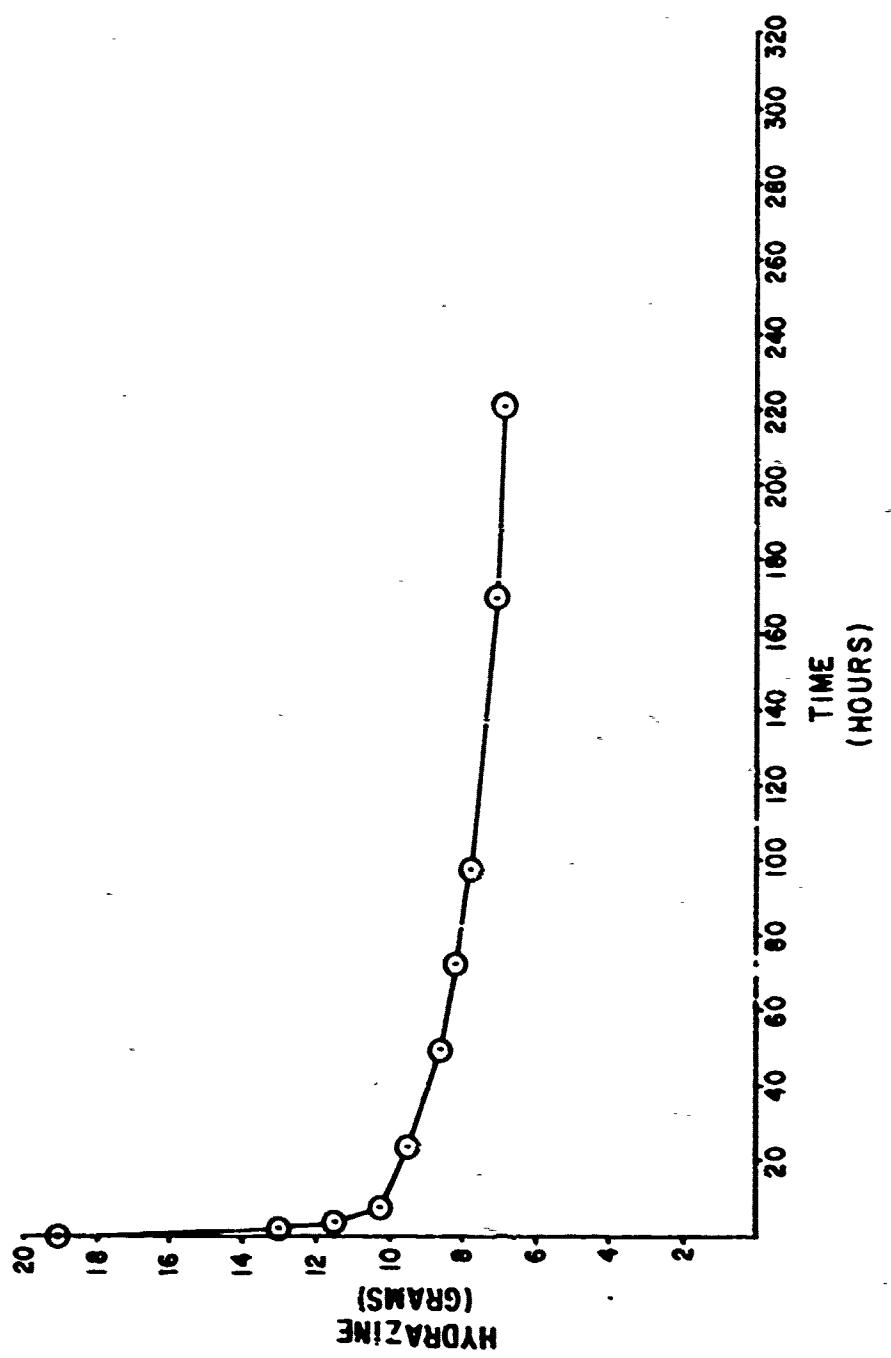
Figure 8. Long-term Evaporations of Hydrazine Fuel

18
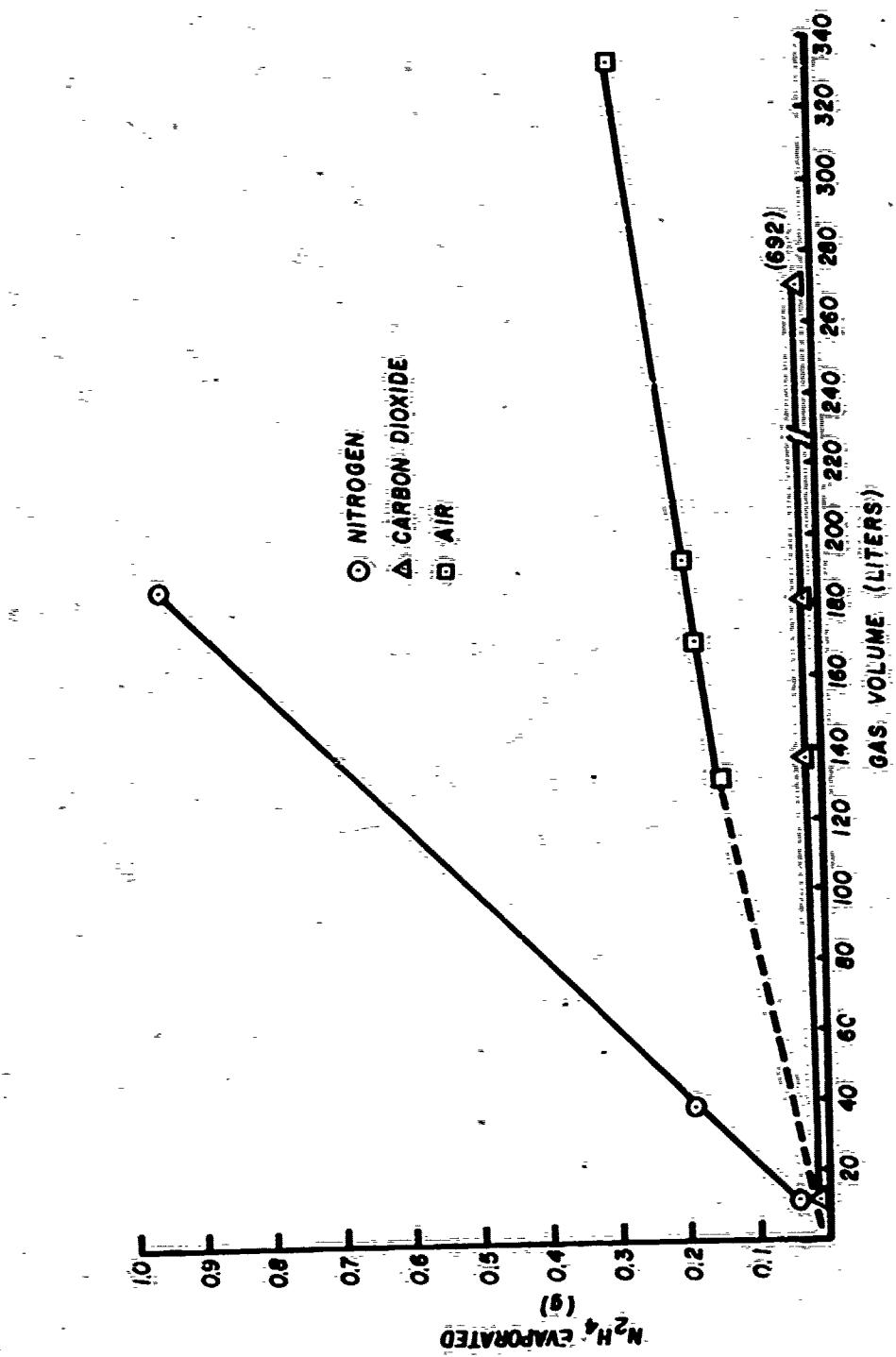
Figure 9. Effect of Different Gases on Hydrazine Evaporation

NITROGEN
CARBON DIOXIDE
AIR

N_2H_4 EVAPORATED (g)

GAS VOLUME (LITERS)

i.e., no correction factor was applied to the data to make up for the 4 to 5 percent discrepancy.

Recoveries of N_2H_4 from concrete surfaces by wiping with felt squares ranged from 5 to 13 percent of the applied hydrazine. The appearance of the felt showed that it was not absorbing much of the hydrazine. Addition of PDAB to the concrete surface gave a bright orange color indicating that hydrazine remained which was not being picked up by the felt. To determine how much additional hydrazine could be recovered from the concrete, the surface was washed with water and the resulting solution showed recoveries of 32 to 73 percent of the amount of hydrazine originally applied.

A concrete surface was exposed to 2.0 ml of 75 percent N_2H_4 solution and then mopped with felt and the surface flushed with water. This sample was placed in the volatilization chamber and the gas flow started. In 46 hr 8.8 mg of the residual hydrazine was volatilized from the surface and continued to be a source of contamination.

Treatment of Dilute Hydrazine Waste Solutions

The following equations represent reactions of hydrazine with the three tested oxidizing agents.

1. $N_2H_4 + 2NaOCl \longrightarrow N_2\uparrow + 2H_2O + 2Na^+ + 2Cl^-$

2. $N_2H_4 + Ca(ClO)_2 \longrightarrow N_2\uparrow + 2H_2O + Ca^{2+} + 2Cl^-$

3. $N_2H_4 + 2H_2O_2 \xrightarrow{Cu^{++}} N_2\uparrow + 4H_2O$
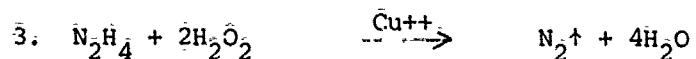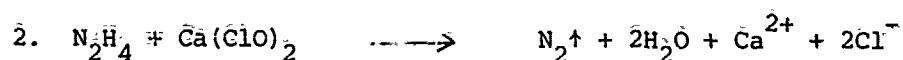
Using these equations, the amounts of oxidizing agent required for stoichiometric reaction with hydrazine may be computed. These amounts are given in Table 3 for anhydrous hydrazine and for H-70 (70 percent

20

hydrazine in water), the fuel used to power the F-16 EPU. It should be noted that the products formed in these reactions are inert salts and nitrogen gas and can be discharged with no environmental consequences.

TABLE 3.   STOICHIOMETRY OF HYDRAZINE OXIDATION

Oxidizing Agent	Amount Required for Stoichiometric Reaction
5.25 percent NaOCl	88 ml per ml neat hydrazine
	62 ml per ml H-70
HTH (65 percent $Ca(ClO)_2$)	6.9 g per ml neat hydrazine
	4.9 g per ml H-70
30 percent (with 10^{-4} M Cu^{++})	7.1 ml per ml neat hydrazine
	5.0 ml per ml H-70

As shown in Figures 10, 11 and 12 the calculated amounts of oxidant are equal to those found experimentally. Since determination of the actual spill volume is difficult excess oxidant should be added to insure complete neutralization.

21

Figure 10. Treatment of Dilute Hydrazine Solution with HTH

hydrazine in water), the fuel used to power the F-16 EPU. It should be noted that the products formed in these reactions are inert salts and nitrogen gas and can be discharged with no environmental consequences.

TABLE 3.   STOICHIOMETRY OF HYDRAZINE OXIDATION

Oxidizing Agent	Amount Required for Stoichiometric Reaction
5.25 percent NaOCl	88 ml per ml neat hydrazine
	62 ml per ml H-70
HTH (65 percent $Ca(ClO)_2$)	6.9 g per ml neat hydrazine
	4.9 g per ml H-70
30 percent (with 10^{-4} M Cu^{++})	7.1 ml per ml neat hydrazine
	5.0 ml per ml H-70

As shown in Figures 10, 11 and 12 the calculated amounts of oxidant are equal to those found experimentally. Since determination of the actual spill volume is difficult excess oxidant should be added to insure complete neutralization.

Figure 11. Treatment of Dilute Hydrazine Solution with Household Bleach
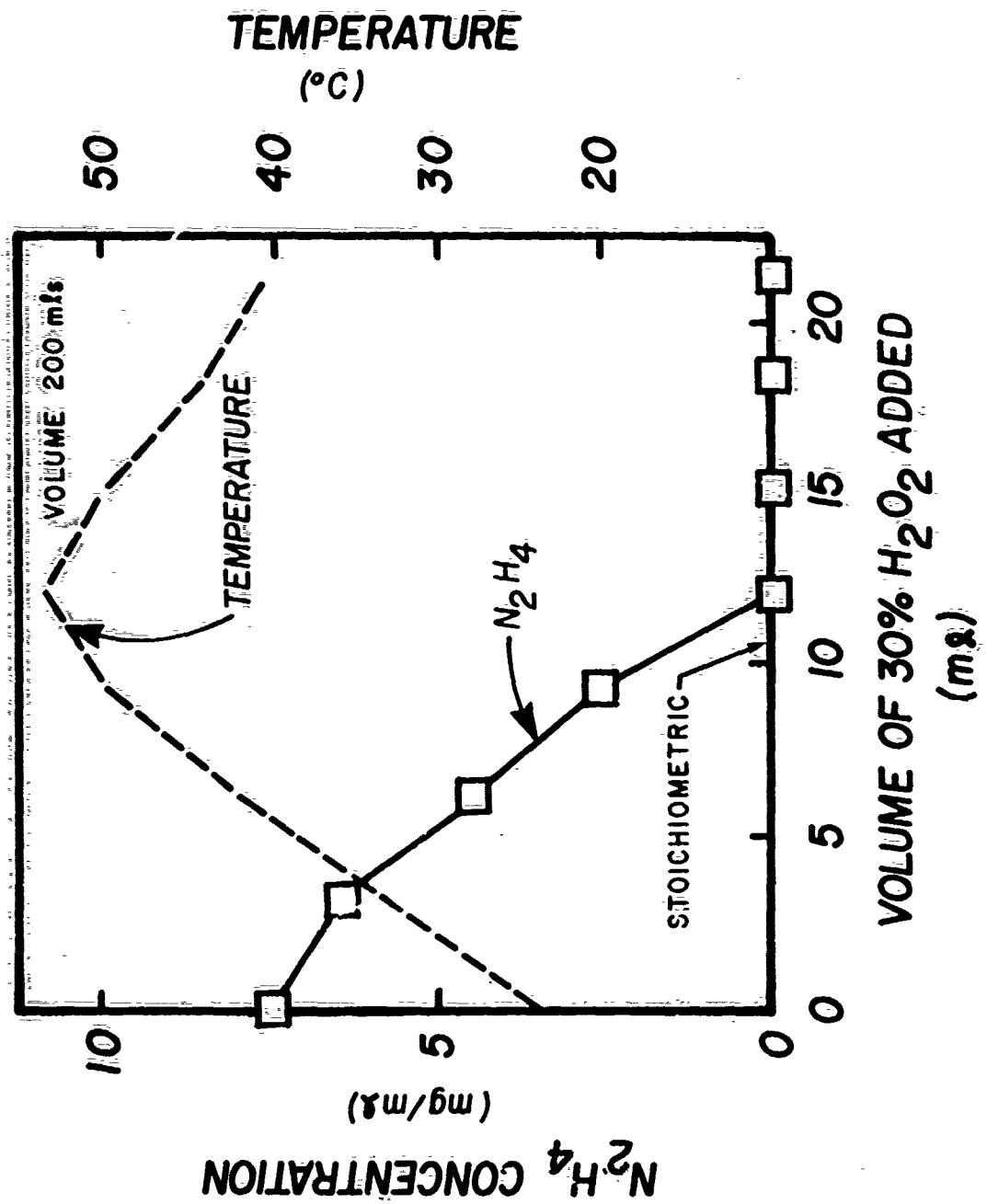
Figure 12. Treatment of Dilute Hydrazine Solution with 30 Percent H_2O_2 in the Presence of $10^{-4}M$ Cu^{++}

SECTION IV

DISCUSSION

Evaporation Studies

The varied evaporation rates observed for the fuel placed outside are indicative of environmental effects on the volatilization rate. In the course of these studies the temperature ranged from 70 to 85°F with 0 to 15-mile-per-hour (mph) winds. Relative humidity was 60 to 85 percent, and the sky was generally clear. It is expected that lower temperatures would decrease the evaporation rates and higher temperatures would increase these rates. Laboratory tests are currently underway to evaluate the magnitude of temperature affects. Relative humidity may also play an important role in the evaporation rate by diluting the fuel during hydration.

Since the evaporation rates observed in the shade were considerably slower than those observed in the other outside studies, several quartz vessels of hydrazine were placed in both the sun and shade. The hydrazine concentrations measured in the vessels showed no difference from sun or shade, therefore indicating that the increased rates were not due to decomposition by ultraviolet light. The increased rates were probably due to solar insolation and the resulting increased solution temperature. This is particularly important in cases where fuels were spilled or hot runways in the sun. Evaporation rates could be much higher than reported here.

The inside studies were conducted exclusively in a laboratory fume hood due to the toxic nature of N_2H_4. The 63.5-cm/sec air velocity at the surface corresponds to a wind velocity of 1.4 mph. These studies represent evaporation under relatively calm conditions. Since all the tests were conducted at the same air velocity, the results are consistent and can be used for comparative studies. Several trials at elevated temperatures were attempted, and preliminary results indicated more

25

rapid volatilization. Problems associated with temperature control necessitated operating at room temperature for these studies. The most important finding from these studies is that hydrazine volatilizes at a sufficiently rapid rate to quickly contaminate surrounding air to a level above the threshold limit value. For example, the inside studies with the neat fuel showed that enough N_2H_4 had evaporated in several hours to contaminate the air in a large closed hangar.

The phenomenon of water absorption by hydrazine pools is not fully understood but is probably due to the formation of hydrazine hydrate. Since the hydrazine continues to evaporate and the weight increases, peaks, and then decreases, there are probably two competing processes involved, i.e, evaporation and hydration. No attempt was made to separate these processes or evaluate the effect on evaporation since the main objective of this study was to observe evaporation rates under real world conditions. Dilution of the fuel with water results in a sub-stantial reduction in the evaportion of hydrazine. This is important since initial dilution of a spill could reduce the potential exposure of personnel downwind of the release. In deciding the appropriate dilu-tion, trade-offs between containment and vaporization must be considered.

The density increase can best be explained in terms of the CO_2 absorption. It is felt that the compound formed is carbazic acid as shown in Equation (3).

$$N_2H_4 \;+\; CO_2 \;\text{---->}\; H_2N\overset{\overset{\displaystyle H}{|}}{N} - C\overset{\displaystyle \nearrow O}{\searrow_{OH}} \tag{3}$$
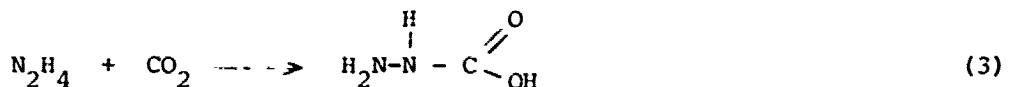
The stoichiometry of the reaction requires a 1:1 molar ratio, but in this study the observed molar ratio was 1.0 mole N_2H_4 to 0.64 moles CO_2. The reaction in this system was probably incomplete, and hydrazine probably evaporated to some extent, therefore, showing low results for the CO_2 absorbed. The effects of reaction 3 under environmental conditions appear to be minor as shown by the slowly increasing density data only

26

in the long-term experiments. Over long periods carbazic acid may act to stabilize the N_2H_4 and reduce the evaporation rate, however, for short periods of time, less than 24 hours, the effect on evaporation should be negligible.

The volatility chamber studies essentially corroborate the CO_2-carbazic acid theory. CO_2 gas volatilized essentially no N_2H_4, and N_2 gas volatilized the most. Air volatilized an intermediate amount as would be expected since it contains some CO_2. It appears that the air curve in Figure 9 may be a little low when compared to the N_2 curve, indicating that the oxygen in the air may be oxidizing the hydrazine to some limited extent. Further studies are planned to determine the affect of different concentrations of CO_2.

Evaluation of Felt Wipes

The felt cleanup procedures were primarily examined for cleaning up small hydrazine spills that could occur while servicing the EPU on the F-16. The felt itself is compatible with hydrazine and absorbs an adequate quantity of pooled hydrazine; however, in the bench studies the problem of cleanup is that the spilled N_2H_4 spreads over the surface and does not pool. Thus the concrete surface merely becomes wetted or damp and it is very difficult to absorb the spilled N_2H_4. Since any hydrazine not removed from the surface will continue to volatilize as shown in the volatility chamber experiments it is necessary that the surface be chemically neutralized, as discussed below, to prevent further volatilization. The lack of 100-percent recovery of applied hydrazine by rinsing with acid solutions indicates that something in the concrete itself may cause some decomposition of the hydrazine. Further work is underway to corroborate this observation.

27

Treatment of Dilute Hydrazine Waste Solutions

The use of hydrazine on the F-16 raises the possiblity of spills of
this material on the flightline area. The general procedure recommended
to the F-16 SPO by CEEDO is a "mop and sop" procedure whereby as much of
the spilled fuel as possible is picked up, diluted with water and
treated with hypochlorite before disposal to the sewer system. The
detailed recommendations sent to the F-16 System Program Office (SPO)
are given in Appendix A.

For small spills (a few drops to a few milliliters), 5 percent
sodium hypochlorite is a suitable oxidizing agent. For larger quantities,
the more concentrated solid HTH (65 percent available chlorine) is
acceptable. However, HTH has the disadvantage of producing an insoluble
sludge which makes ultimate disposal more inconvenient. At no time
should pure hydrazine or H-70 fuel be allowed to come into direct contact
with either HTH or 5 percent sodium hypochlorite solution. The possible
result would be an explosive reaction with flames.

Hydrogen peroxide is also a good oxidizing agent for dilute hydra-
zine solutions, however, a catalyst is required to cause the reaction to
proceed at a reasonable rate. Also, care must be taken to insure that
the copper catalyst is added prior to adding the H_2O_2 to avoid vigorous
gas production and spraying of the solution. A commonly available
copper salt suitable for use is cupric sulfate hexahydrate, $CuSO_4.6H_2O$.
Approximately 27 mg of this salt should be added for each liter of waste
solution to be treated or about 0.1 g per gallon.

The approximate current prices on a cost per equivalent (eq/ml
N_2H_4) basis are given in Table 4. These will vary considerably from one
location to another. Because of its ready availability, household
bleach is recommended for small spills. A gallon of bleach is enough to
oxidize approximately 60 ml of H-70 fuel. For larger spills, the volume

28

of bleach becomes unwieldly, and either HTH or 30 percent H_2O_2 should be used. Again, because of its ready availability and long shelf life, HTH is recommended. Since it will be used only rarely in case of fairly large accidental spills, the problem of precipitate formation during treatment is acceptable.

TABLE 4. COST OF OXIDIZING AGENTS

Oxidizing Agent	Cost per Equivalent
5 percent NaOCl	$0.77
70 percent Ca(OCl)$_2$	$0.27
30 percent H_2O_2	$2.34

The reduction of N_2H_4 concentration and rise in temperature for each of the three oxidants is given in Figures 10, 11, and 12. The residual hydrazine concentration in the beaker after a 10-percent excess of each oxidizing agent was not detectable by the colorimetric test employed (sensitivity was 50 ppb). The maximum temperature during treatment ranged from 40° to 60^OC. In each case, addition of the oxidizing agent was accomplished over a period of 20 minutes. In the case of hydrogen peroxide, the reaction proceeded only very slowly in the absence of a catalyst. In the presence of $10^{-4}M$ cupric ion, however, the reaction proceeded vigorously.

After addition of each aliquot of oxidizing agent, vigorous bubbling was observed as nitrogen gas was released. In the case of HTH, a white precipitate formed, presumably composed of insoluble calcium salts. In the case of NaOCl and H_2O_2 solutions, the treated waste solution remained clear with a yellow to brown color appearing during the oxidation process.

Since measurement of residual hydrazine is not normal for most installations the evidence of residual chlorine in a well mixed solution

29

or on a pavement spill can be used to determine neutralization. The presence of residual chlorine is easily determined with orthotolidine as described in the attached procedures.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

The studies reported here illustrate that hydrazine, although exhibiting a low vapor pressure (14.2 mm Hg at $25^{O}C$), will evaporate at a rate sufficient to establish atmospheric concentrations in excess of permissable levels. As expected, the evaporation rate is faster in the sun and at higher temperatures. Both dilution and adsorption of carbon dioxide decrease the evaporation rate. Both adsorption of water and carbon dioxide cause a reduction in the evaporation rate over a long period of time.

Cleanup of spilled hydrazine with polyethylene felt or other materials on concrete is not complete and the residual hydrazine must be neutralized with hypochlorite or hydrogen peroxide. Tests with three oxidants, NaOCl, $Ca(OCl)_2$ and H_2O_2 showed that hydrazine is oxidized with stoichiometric amounts of the agent. It is recommended that due to availability and ease of handling, sodium hypochlorite (household bleach) be used for small spills and calcium hypochlorite be used for larger spills. Step-by-step procedures for cleanup are included in Appendix A.

REFERENCES

1. Rose, Arthur and Elizabeth, The Condensed Chemical Dictionary, 5, 568, (1956).

2. "Storage and Handling of Aqueous Hydrazine Solutions," Olin Corporation, Stanford, Connecticut.

3. Criteria Document: Recommendations for an Occupational Exposure Standard for Hydrazines, National Institute for Occupational Safety and Health (9 September 1978).

4. Marsh, W. R. and Knox, B. P, USAF Propellant Handbook Hydrazine Fuels, AFRPL-TR-69-149 (1970).

5. Vogel, Arthur I., Quantitative Inorganic Analysis, 3, 380 (1961).

6. Pesez, M., and Petit, A., "Recherche et dosage del' hydrazine," Bulletin de la Societe Chimque de France, 122, (1947).

7. Watt, G. W. and Chrisp, J.D., "A Spectrophotometric Method for the Determination of Hydrazine," Anal. Chem. 24, 2006 (1952).

8. Dee, L. A., "Gas Chromatographic Determination of Aqueous Trace Hydrazine and Methylhydrazine as Corresponding Pyrazoles," Anal. Chem. 43, 1416 (1971).

9. MacNaughton, M.G. et. al, "Oxidation of N_2H_4 in Aqueous Solution," CEEDO-TR-78-11 (1977).

APPENDIX A

RECOMMENDATIONS FOR CLEAN-UP OF H-70 FUEL SPILLS

1. With regard to cleaning up any spill of hydrazine, there are several general considerations that must be kept in mind:

a. The procedures outlined below are appropriate for accidental spills of hydrazine on the flightline ramp or hangar area such as might occur with a broken H-70 tank fitting or leaking fuel line. For the purposes of this document, the word, "spill", does not include the anticipated release of small quantities (drops) for which preventive measures have been taken (see paragraph 4a).

b. The general idea is to mop up as much of the hydrazine as possible, neutralize any remaining damp spots, and flush the area with water. In those locations such as the H-70 tank-refilling station where floors and drainage systems have been designed to include a holding sump, it is most expedient to immediately flush a spill with water into the holding sump for subsequent treatment and release. However, there is no way to be sure that such a holding sump will always be available, and it may not be advisable to flood the aircraft compartments with water. The mop-up procedures recommended below provide a generally applicable technique for cleaning up accidental spills of H-70 in a manner which is manageable and safe for the personnel involved and prevents the release of untreated hydrazine to the environment.

c. All personnel not essential to the clean-up operation should be removed from the area to avoid breathing hydrazine vapors. Care must also be exercised to avoid contact with the skin since hydrazine is readily absorbed through the skin surface. First aid procedures for any contact with hydrazine are to remove the exposed personnel from the contaminated area, thoroughly flush the contacted body areas (eyes, skin, etc.) with water, and summon medical personnel immediately.

d.   No spill cleanup should be attempted until the personnel conducting the cleanup have put on protective clothing.   At this time, in the absence of any official USAF guidance, the use of self-contained breathing apparatus, gloves, boots, and apron should be considered a minimum.

e.   All possible care must be taken to avoid release of hydrazine to the environment until it has been neutralized.   Hydrazine is toxic at the ppm level to aquatic life, and simply flushing a spill into the storm drain or sanitary sewer could result in disastrous consequences.

2.   The following materials will be required for accomplishing clean-up and neutralization of H-70 spills:

a.   Polypropylene felt - This material is manufactured by the GAF Corporation and is available in lots of 500 square yards or more.   It is compatible with hydrazine and has been successfully used by NASA to clean up hydrazine spills.

(1)   Kit for small spill - For wiping up small spills (a few milliliters) and to catch the drops that frequently escape when manipulating tank fittings on the aircraft, this material may be cut into small squares (6 inches x 6 inches) and stored individually in plastic bags until needed.

(2)   Kit for larger spills - For sopping up large spills, bigger strips of felt (e.g., 2 feet x 6 feet) should be used.   A kit of three such strips, rolled up and sealed in a plastic bag, should be immediately available to personnel whenever the H-70 fuel tank is being handled or transported.

(3)   Storage - The pieces of felt should always be stored in sealed plastic bags to exclude dirt, moisture, and other contaminating substances that are found in the flightline environment.

b. Sodium hypochlorite solution, 5 percent (household bleach) - This is an aqueous solution of sodium hypochlorite (NaOCl) and may be used to neutralize concrete surfaces contaminated with hydrazine or to neutralize dilute water solutions of hydrazine mopped up after a spill.

c. Methanol - This material is required only when the ambient temperature during spill clean up is anticipated to be below $0^{\circ}C$ ($32^{\circ}F$). In this case, a 50 percent (V/V) solution is prepared by mixing equal volumes of water and methanol. The resulting solution has a freezing point of about $-50^{\circ}C$ and should be used in place of water during the cleanup procedure.

d. Squeeze bottle - Laboratory-type polyethylene bottle with tapered tip.

e. Large container - This should be large enough to hold the entire contents of an EPU H-70 tank (6.5 gallons) with room for 3-fold dilution. Something like a 30-gallon heavy duty waste container with lid would be adequate. The can should have handles and be sturdy enough to transport while nearly full of water solution. Materials compatible with hydrazine (polypropylene, polyethylene, stainless steel) should be used.

f. Protective clothing - See paragraph 1d.

3. The following procedure is recommended for use with spills of H-70 on concrete surfaces:

a. Clear area of all personnel except cleanup team and summon the Base Bioenvironmental Engineer.

b. Attempt . contain the spill by placing the first pieces of felt on the leading edge of the spill to act as a barrier to further spreading.

35

c. Fuming and fire hazard may be reduced by adding minimal amounts
of water (see paragraph 2c if temperature is below $0^{\circ}C$) to contained
spill. The amount of water to add here is up to the on-site team leader.
A volume of water equivalent to the volume of H-70 spilled would be
sufficient to reduce fuming significantly and render the fuel nonflam-
mable. However, avoid adding too much water as this would increase the
area of the spill, making cleanup more difficult and the likelihood of
environmental contamination greater.

d. Mop up as much of the spilled fuel as possible. This may be
accomplished by moving around the pieces of felt on the spill area until
the felt is saturated with the hydrazine solution. Carefully place the
pieces of felt in the large container (see paragraph 2e) partially
filled with water (or 50-percent methanol/water if below $0^{\circ}C$). The
volume of fluid in the container should be about 10 gallons or enough to
cover the fuel-soaked pieces of felt. The pieces of felt may be squeezed
out over the container and placed down again to soak up more spilled
fuel.

e. Additional hydrazine can be removed from the damp concrete by
adding small quantities of water and mopping up as before.

f. The damp area on the concrete must now be treated by adding
small amounts of bleach. If the ambient temperature is below $0^{\circ}C$
($32^{\circ}F$), the bleach must be mixed with methanol/water solution to prevent
freezing. When excess chlorine can be detected on the spill area using
orthotolidine reagent (see paragraph 5f), the spill can be considered
neutralized. The Base Bioenvironmental Engineer can assist in this
chemical test.

g. Finally, the spill area should be flushed with large amounts of
water. The Base Bioenvironmental Engineer should be involved in the
final stages of clean up to insure that proper neutralization procedures
have been accomplished prior to final flushing.

36

h. In the event that the recommended polypropylene felt material is not available, certain alternative materials may be used. For containing the spill and mopping up, large pieces of clean, white, cotton cloth may be used. Also a clean cotton mop with wooden handle may be used. However, every effort should be made to provide the felt material wherever possible. This will preclude the inadvertent use of dirty wipes or materials incompatible with H-70.

4. For cleaning up spills on the aircraft, the following procedures should be followed:

a. Preventive measures - Where small leaks are likely to occur during maintenance operations, such as when disconnecting H-70 tank fittings, place a piece of the felt under the fitting to catch any drops of H-70 that may be released. If the felt is not available a piece of cotton cheesecloth lightly moistened with water is satisfactory.

b. Spills on the aircraft surface should be sponged up with felt or cloth. Use small amounts of water (see paragraph 3c) from a squeeze bottle or rinse down the contaminated area on the aircraft, sponging these up with a clean piece of felt or cloth.

c. The pieces of felt or cloth should be placed into a container of water (see paragraph 3c if temperature is below 0°C) for later decontamination. If the amount of hydrazine on the wipes is small (several drops), they may also be placed directly into a container of bleach. Such a container of bleach will usually be available during maintenance operations on the EPU fuel tank. CAUTION: Only small amounts of hydrazine (drops) should be placed directly into bleach solution.

5. Once the spill has been cleaned up, the container of diluted hydra-
zine fuel must be neutralized before release. The solution may be
treated with the felt wipes present in the container, discarding the
wipes after treatment. The following procedures apply to the neutraliza-
tion process:

a. The hydrazine waste solution should be diluted with water until
the estimated concentration of hydrazine is less than one percent. It
may be necessary to transfer successive portions of the waste solution
to another container in order to achieve this dilution, neutralizing
each portion separately. The neutralization procedure should be carried
out in a well ventilated area where the ambient temperature is above 0°C
(32°F).

b. Either commercial granular HTH (65-percent Ca(ClO)$_2$) or household
bleach solution (5-percent NaClO) can be used to neutralize dilute
solutions of hydrazine. The household bleach is recommended because of
its dilute concentration, availability, and lack of controlled storage
requirements. HTH has the advantage of being more concentrated, thus
requiring less material for neutralization. However, HTH must be
handled with extra caution since it contains a higher concentration of
hypochlorite, thus reacting more vigorously with the hydrazine. Also,
the use of HTH produces a deposit of insoluble salts in the container
after treatment, making final disposal more inconvenient.

c. Estimating the quantity of neutralizing agent required will be
different for the two materials described in paragraph 5b. The quantities
specified below include enough material to neutralize the hydrazine
present and provide a 10-percent excess of hypochlorite.

(1) Five-percent hypochlorite solution (household bleach) -
For each volume of H-70 spilled, use 100 volumes of bleach. For example,
assume the volume of a spill is estimated to be about one pint of H-70
fuel. The volume of bleach required will be about 100 pints (12.5
gallons).

38

(2) Commercial HTH (65-percent calcium hypochlorite, granular) -
For each gallon of H-70 spilled, use about 42 pounds of HTH. In metric
units, for each milliliter of H-70 spilled, use 5 grams of HTH. For
example, assume that the volume of a spill is estimated to be about one
pint of H-70 fuel. The weight of granular HTH required will be 42/8 =
5.25 pounds (1 pint = 1/8 gallon).

d. The decision of which agent to use for neutralization will
depend on the volume of H-70 spilled. For small spills (less than a
quart), the use of household bleach is recommended. For larger spills,
the volume of bleach required becomes unmanageable, and it is preferable
to use the more concentrated agent, HTH. For example, assume it is
necessary to neutralize the entire contents of an H-70 fuel tank (6.5
gallons). This would require 650 gallons of bleach or 272 pounds of
HTH. In either case the task of neutralization will be difficult, but
the storage space required for the bleach solution is much greater than
for the equivalent amount of HTH.

e. Before adding bleach or HTH, the hydrazine waste solution (or
portion thereof) must be diluted with water until the concentration of
hydrazine is about one percent. HTH or bleach should then be CAUTIOUSLY
added in small increments while stirring the solution continuously. A
vigorous bubbling action will be observed as the hydrazine is oxidized
to nitrogen gas and the solution will become warm.

f. When there is no further bubbling on addition of bleach or HTH,
the hydrazine is probably completely oxidized. To be certain, it is
necessary to determine if there is a chlorine residual using orthotolidine
reagent.

(1) To check for neutralization, 20 milliliters of the treated
waste should be collected and 1.0 milliliter of orthotolidine reagent
added. A bright reddish orange colored solution indicates excess chlorine,

39

and the neutralization is complete. A colorless or yellow solution
indicates that more HTH or bleach is required. Add more bleach or TH
to the well mixed waste solution and repeat the test until a reddish
orange color is obtained.

(2) The orthotolidine solution is prepared by dissolving 1.35g
of orthotolidine dihydrochloride in 500 l distilled water and adding a
mixture of 250 mls concentrated hydrochl·ic acid and 350 ml distilled
water. Store in dark brown bottles. Replace after six months. This
solution is available premixed as Federal Stock No 6810-00-270-8289.
This reagent is toxic and should be handled carefully.

g. The treated waste solution may usually be released to the
sanitary or industrial waste sewer system. Before final disposal of the
treated waste solution, consult the base Bioenvironmental Engineer to
insure that proper procedures are followed. Before disposing of the
solution in a storm sewer it may be necessary to neutralize the excess
chlorine with thiosulfate until a negative test for chlorine is obtained
with orthotolidine.

7. In the unlikely situation (such as fire) that the area must oe
flushed with water after a spill, base CE personnel must be notified
immediately to attempt to isolate the spill in the system prior to
reaching any on-base or off-base area where aquatic life is present.
The stopped flow should be treated with bleach as above, tested for
excess chlorine residual, and then dechlorinated with sodium thiosulfate.
The Base Bioenvironmental Engineer should be called before any of the
contained liquid is released.

INITIAL DISTRIBUTION

ADTC/CZ	1	HQ MAC/SGPE	1
DDC/TCA	2	HQ MAC/DE	1
HQ AFSC/DL	1	HQ PACAF/SGPE	1
HQ AFSC/SD	1	HQ PACAF/DLMU	1
HQ USAF/LEEV	1	HQ AFISC/SES	1
HQ USAF/SGPA	1	HQ ATC/SGPAP	1
OSAF/MIQ	1	SAMTEC/SEM	3
OSAF/OI	1	AFTAC/TRA	1
AFIT/Library	1	OG-ALC/SGP	1
AFIT/DE	1	SA-ALC/SFQT	1
Federal Laboratory Program	1	SAARM/QA	1
EPA/ORD	1	USA Environ Hygn Agency/ENGMC-RD	1
USA Chief, R&D/EQ	1	USAMBRDL	1
USN Chief, R&D/EQ	1	Naval Air Propulsion Center	1
OEHL/CC	3	ARPA	1
AFETO/DEV	1	DD-MED-41	1
USAFSAM/EDE	2	USAF Hospital/SGB	1
HQ AFISC	2	Hill AFB UT 84406	
AUL/LSE	1		
HQ USAFA/Library	1	USAF Hospital/SGP	1
Det 1 ADTC/TST	1	Edwards AFB CA 93523	
1 MSEW	1		
OUSDR&E	1	USAF Hospital/SGP	1
USAF Hospital, OEHL	3	Eglin AFB FL 32542	
AMD/RD	1		
AMRL/THE	1	USAF Hospital/SGP	1
USAFSAM/VNL	1	Vandenberg AFB CA 93437	
AFRPL/Library	1		
AFRPL/LKDP	1	Det 1 ADTC/CC	1
ASD/YPL	1	Det 1 ADTC/ECC	15
AFOSR/NC	1	AFIT/LSGM	1
FTD/LGM	1		
ADTC/DLODL (Tech Library)	1		
AFWL/SUL (Tech Library)	1		
SAMSO/DEV	1		
SAMSO/LV-1	5		
HQ AFSC/SGPE	1		
HQ AFSC/DEV	1		
HQ TAC/SGPB	1		
HQ TAC/DE	1		
HQ SAC/DEP	1		
HQ SAC/SGPA	1		
HQ USAFE/SG	1		
HQ USAFE/DEPV	1		